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(Commemoration Issue Dedicated to Professor Ken-ichi Katayama On the Occasion of His Retirement)

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The Deformation of the Nearly Perfect Crystals of Polydiacetylene (PTS)*

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The single crystals of polydiacetylene (PTS) polymerized in solid state from the monomer crystals have been studied by X-ray topography, optical microscopy and scanning electron microscopy. The crystal is found to be nearly perfect. Dislocations in the polymer crystal have been inherited from the monomer crystal. The dislocations do not play an important role in plastic deformation such as bending and compression along the polymer chain. The deformation occurs mainly by twinning; two kinds of composition plane of twin have been observed: (120) and (12 $\bar{2}$). Both of the twins have shear component perpendicular to the chain direction; the twinings require chain kinking as well as the rearrangement of disposition of the chains with large side groups. The possible mechanisms of the twinings are discussed.

KEY WORDS: Polydiacetylene / PTS / Twin / X-ray topography / Lattice Defects / Plastic deformation

1. INTRODUCTION

The plastic deformation of polymer crystals has been investigated mostly on semi-crystalline polymers. They are the mixture of small crystals and amorphous parts; mechanical properties such as plasticity depend on the state and distribution of the amorphous parts. Hence, the interpretation of the deformation of polymer crystals may be ambiguous.

The extended chain crystals of polyethylene¹⁾ and copolymers of vinylidene fluoride and trifluoroethylene²⁾ have been found to have essentially no amorphous parts. Polyoxymethylene crystals polymerized in solid state have been reported to be perfect.³⁾ They are, however, still of the order of μm in size.

Recently it has been reported that a kind of polydiacetylene, the polymer of 2, 4-hexadiyne 1,6-diol bis (para-toluene sulphonate) (PTS), can be obtained to be a perfect crystal of cm in size by the solid state polymerization of the monomer crystal.⁴⁾ The polymer has mainly acetylenic backbones ($=\text{CR}-\text{C}\equiv\text{C}-\text{CR}=\text{}$) with a large side group R of $-\text{O}-\text{SO}_2-\text{C}_6\text{H}_4-\text{CH}_3$; some parts have been reported to have butatrienic back bones (Fig. 1)⁵⁾ The crystal structure of PTS polymer has been determined by Kobelt and Paulus⁶⁾: monoclinic ($P2_1/c$) with $a=1.449\text{nm}$, $b(\text{chain direction})=0.491\text{nm}$, $c=1.494\text{nm}$ and $\beta=118.1^\circ$.

Izumi et al⁷⁾ investigated the lattice defects of PTS crystals by X-ray topography; the dislocations in the polymer crystals have been found to be the heritage from the

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Deformation of the Nearly Perfect Crystals of Polydiacetylene (PTS)

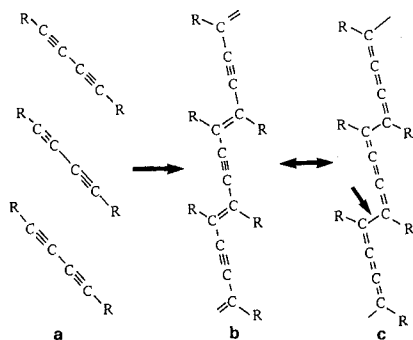


Fig. 1 Back bone structure of PTS. a): diacetylene; b): polydiacetylene (acetylenic structure); c): polydiacetylene (butatrienic structure).

monomer crystals. Young et al.⁸⁾ reported that the plastic deformation of the crystal occurred by twinning and they determined the elements of the twinings.

The present paper reports the study of the deformation of nearly perfect PTS crystals by X-ray topography, X-ray diffraction, scanning electron microscopy (SEM) and optical microscopy with a video system.

2. EXPERIMENTAL

The single crystals of PTS monomer were grown from acetone solution at 4°C by evaporation of solvent. The solid state polymerization was carried out by thermal polymerization at 60°C for 3 days. The colour of the crystal changes with polymerization from transparent pink to glossy gold through pale red and dark red.

X-ray topographs were taken by a conventional Lang camera with $CuK\alpha_1$ radiation. The crystals were plastically deformed by indentation on the surface or edge of the crystal, and the bending and compression which cause the kinking of polymer chains in the crystal. The crystallographic relationship between the twin and matrix was investigated by Laue photographs. A scanning electron microscope JEOL 25S II was used for the observation of fine structure of the twins. The in situ observation of the formation and growth of the twins was done for compression along the chain axis with an optical microscope and recorded on video tape.

3. RESULT

The PTS monomer crystals obtained have well-developed (100) surfaces. The Lang topograph of the polymerized crystal shows that several dislocations exist (Fig. 2, 3); their Burgers vectors are $\langle 211 \rangle$, $[010]$ and $[001]$. They have been inherited from the monomer crystal. No dislocation in the polymer crystal moves under the deformation performed, indentation and bending (Fig. 2, 3); the polymer crystal was plastically deformed only by twinning. Two types of twin were observed in the present deformation by bending and uniaxial compression. These two twins have the same crystallography as that reported by Young et al.⁸⁾

The (120) twinning occurred easily by the deformation mode which bends the chain in the crystal. The twin has smooth surface and forms a clear band on the (100)

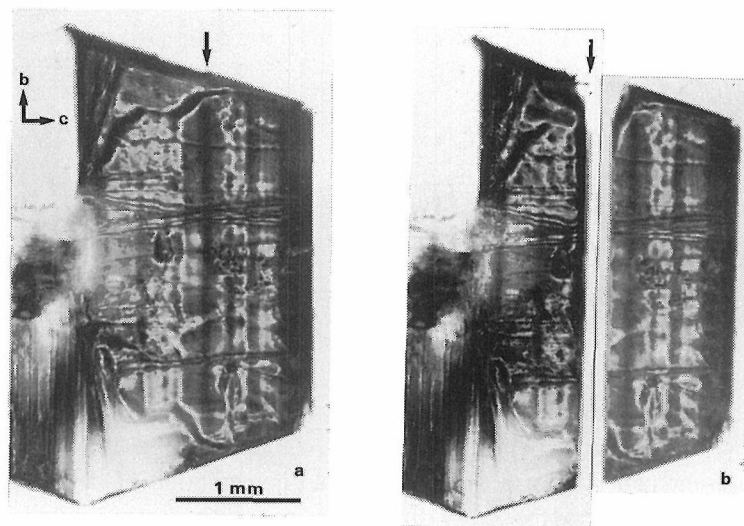


Fig. 2 X-ray topographs of a PTS polymer crystal by $10\bar{2}$ reflection. a): as polymerized; b): after the indentation on the crystal edge pointed by an arrow. The dislocations nearly parallel to $[001]$ have a $[001]$ Burgers vector, and those parallel to $[010]$ have a $[010]$ or $[001]$ Burgers vector. All the dislocations lie on the (100) plane. The crystal fractured along b axis. The dislocations do not change their shape and number.

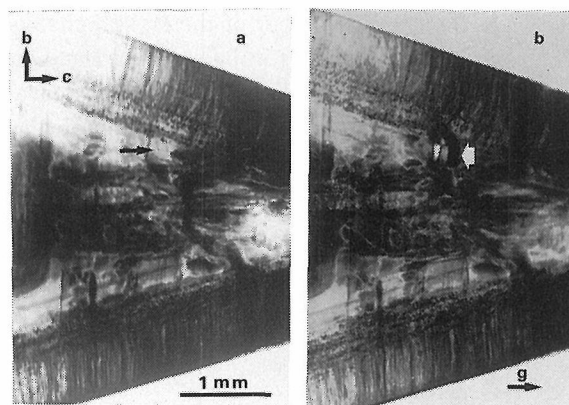


Fig. 3 X-ray topographs of a PTS polymer crystal by $10\bar{2}$ reflection. a): as polymerized; b): after the indentation at the arrowed point. The dislocations do not change their position, number and shape.

surface with a constant width along the trace $[001]$ of the composition plane (Fig. 4). The twin boundary is sharp and narrow, less than $0.1 \mu\text{m}$; the chain must kink cooperatively along the shear direction. The Laue photograph shows sharp reflection spots of both the twin and matrix, and confirms that the (120) twin has the exact crystallographic relationship with the matrix (Fig. 5). The X-ray topograph also shows that twin boundaries are sharp; the matrices of both sides of the twin satisfy the exact Bragg condition (Fig. 6). Hence, the mother lattices suffer no strain by the twinning.

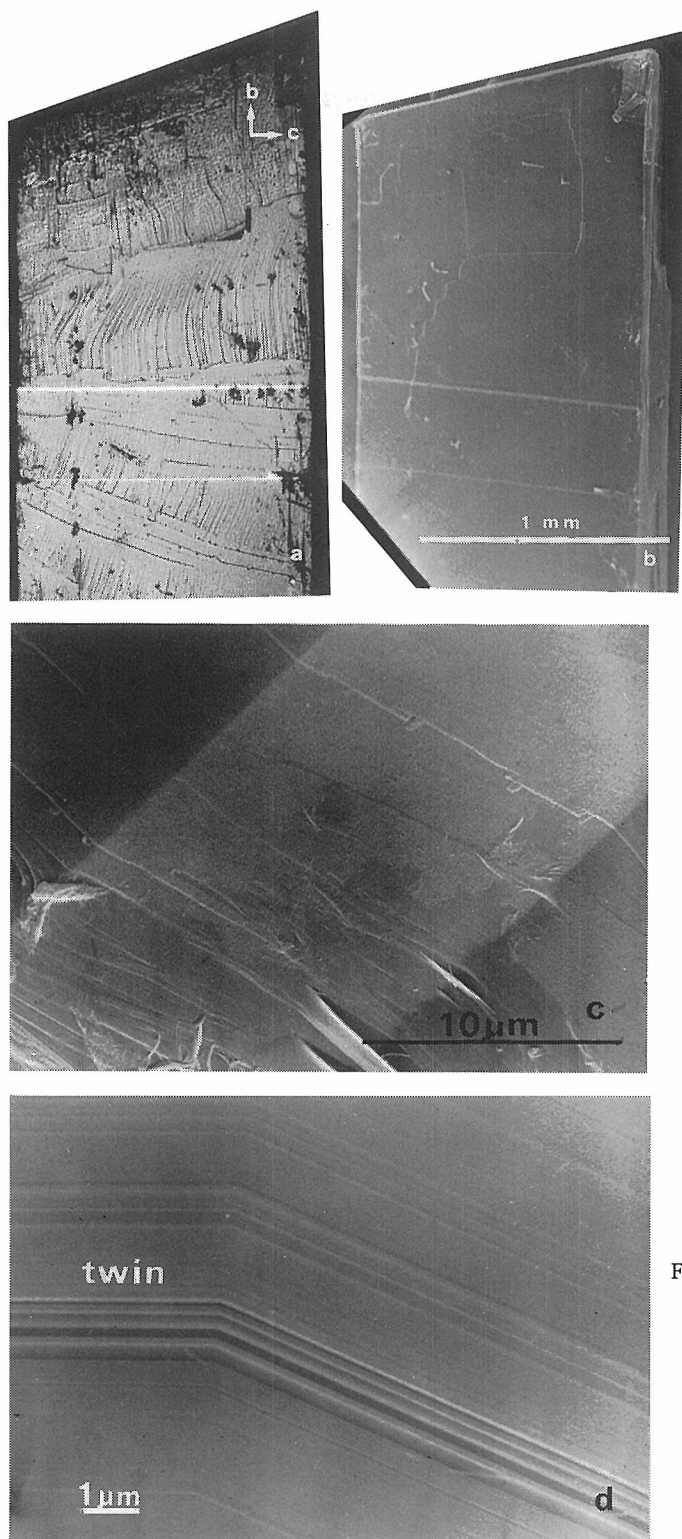


Fig. 4
(120) twinned PTS polymer crystal. a): reflection optical micrograph. b): Scanning electron micrograph of the same crystal as a); c): Scanning electron micrographs. Viewing direction is normal to the (100) plane and d) parallel to the (001) plane.

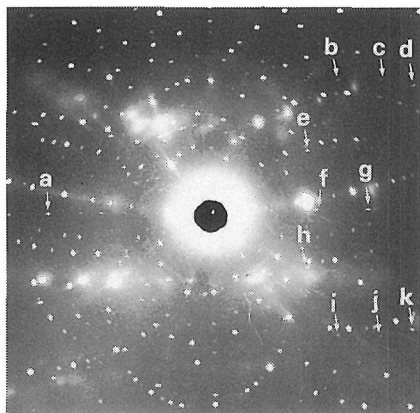


Fig. 5 Laue Photograph of a (120) twinned PTS polymer crystal. Incident X-ray beam is normal to (100) plane of the twin. Several of small sharp spots from (120) twin are indexed. a: $3\ 0\ \bar{4}$; b: $0\ 3\ 9$; c: $0\ 3\ 13$; d: $0\ 3\ 16$; e: $\bar{1}\ 1\ 5$; f: $\bar{1}\ 0\ 4$; g: $\bar{1}\ 0\ 6$; h: $\bar{1}\ \bar{1}\ 5$; i: $0\ \bar{3}\ 9$; j: $0\ \bar{3}\ 13$; k: $0\ \bar{3}\ 16$

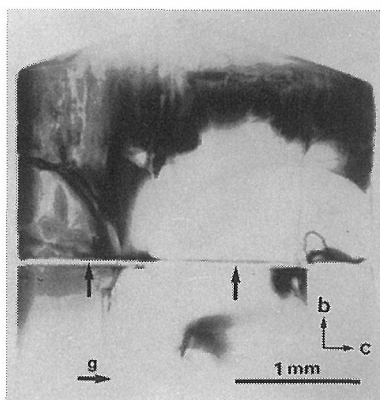


Fig. 6 X-ray topograph of (120) twin of PTS polymer crystal by $10\bar{2}$ reflection. The twin is pointed by arrows. The twin boundaries are sharp; both sides of the twins satisfy the exact Bragg condition.

The conjugate plane, K_2 plane, of this twin is the (100) plane, the surface of the crystal, and hence the rearrangement of the surface is not required for the (120) twinning.

Another twinning, the $(12\bar{2})$ twinning, did not occur by the bending but occurred only by compression along the chain axis. The twin boundary is again sharp and narrow (Fig. 7). The X-ray topograph shows that the mother matrices are not deformed by the twinning (Fig. 8). The K_2 plane is the $(10\bar{2})$ plane; the surface of the crystal has to be rearranged.

The in situ observation of twinning process revealed the difference of the formation and growth between the two twinings. The (120) twin with parallel twin boundaries can grow very rapidly, i.e. in a time interval less than the time resolution of the video system, $1/30$ s for one frame (Fig. 9). On the other hand, the $(12\bar{2})$ twin grows relatively slowly; both the width and length of the twin increase with compression strain (Fig. 10). The twin boundary is not always parallel.

4. DISCUSSIONS

The plastic deformation of crystals generally occurs by slip, twinning and phase transition such as the Martensite transformation. In particular, slip by dislocation is

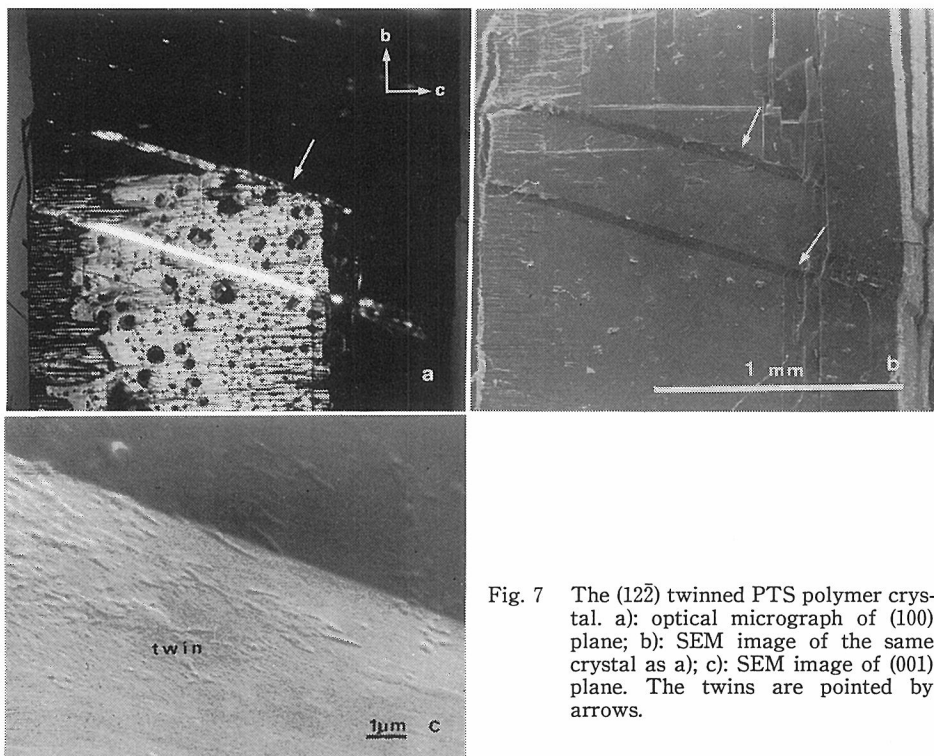


Fig. 7 The $(12\bar{2})$ twinned PTS polymer crystal. a): optical micrograph of (100) plane; b): SEM image of the same crystal as a); c): SEM image of (001) plane. The twins are pointed by arrows.

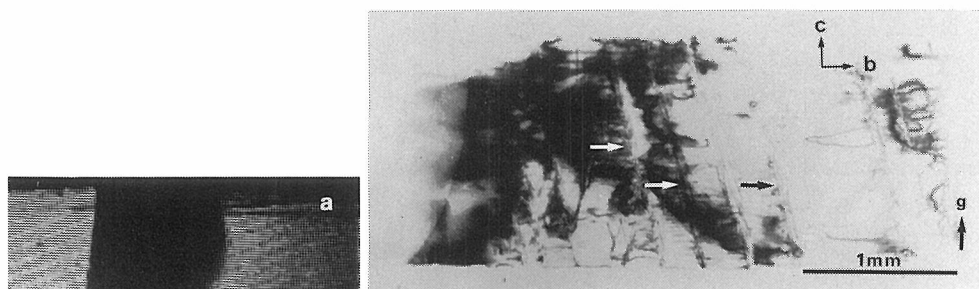


Fig. 8 X-ray topograph of $(12\bar{2})$ twinned PTS polymer crystal by $10\bar{2}$ reflection. Twins are pointed by arrows.



Fig. 9 Optical micrographs of (120) twinning induced by compression along b axis (horizontal). The last number is frame number in a unit of $1/30$ s. The twin has formed in one frame (less than $1/30$ s).

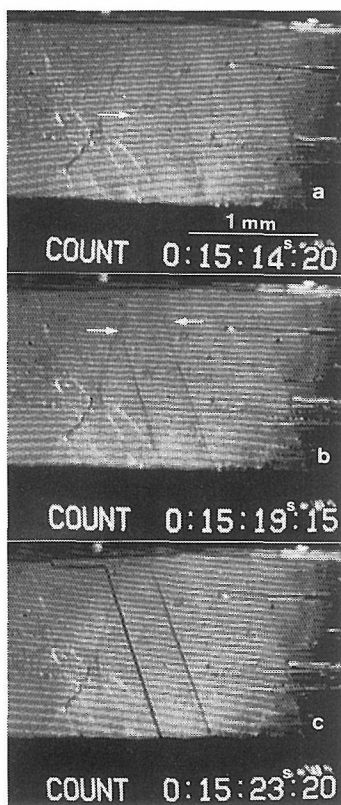


Fig. 10 Optical micrographs of $(12\bar{2})$ twinning induced by compression along b axis (horizontal). Twins needed a few seconds to propagate.

the most important mode of the plastic deformation.

However, in PTS polymer crystals, slip by dislocation does not play an important role. Dislocations in PTS polymer single crystals have been inherited from the monomer crystal. Most of the dislocations observed have the (100) slip plane, parallel to the crystal surfaces; their Burgers vector are $[001]$ and $[010]$. The dislocations with the (100) slip plane are glissile except the edge dislocation with the $[010]$ Burgers vector. But they are not important to the deformation performed in the present study, bending, compression or indentation of the surface. Because they can glide only by shear parallel to the (100) plane. Some dislocations have slip planes inclined to the crystal surface: $\{011\}$ and $\{111\}$.⁷⁾ The dislocations with the $\{011\}$ or $\{111\}$ slip plane are sessile and are not introduced in PTS polymer crystals by deformation, because the slip planes are not parallel to the chain axis. However the sessile dislocations in the polymer crystal are able to be inherited from the monomer crystal. The polymerization of PTS is homogeneous and leaves the dislocation structure unchanged.

The monomer crystal fractures by bending or compression along $[010]$; the PTS monomer crystal cannot deform plastically by this type of deformation.

The polymer crystal has more restriction of the molecular motion for the plastic deformation than the monomer crystal because the molecules are bound along the chain axis by covalent bonds. Plastic deformation will be more difficult than that of the monomer crystal. However, the polymer chains have enough strength for the

deformations, and hence they can bend and eventually form the twins without fracture.

Two types of twin were observed; each has the (120) or (12 $\bar{2}$) composition plane. The (120) twin has $[2\bar{2}, 11\ 1\bar{0}]$ shear direction and the (12 $\bar{2}$) twin has $[\bar{2}, 34, 34]$ shear direction.⁸⁾ By bending around the c-axis (perpendicular to the chain axis), only the (120) twinning occurred. On the other hand, the compression along the chain axis produces the both of the twins.

Twinning occurs by resolved shear stress along the shear direction on the composition plane. For the bending the resolved shear stress is much larger for the (120) twin than that for the (12 $\bar{2}$) twin by a factor of 7. However, for the compression the factor reduces to 0.6. Consequently, it can be explained in the light of resolved shear stress that only the (120) twins have occurred by the bending while on the compression both of the twinings have occurred.

The (120) twins propagate across the crystal in a period shorter than 1/30 s. However, the (12 $\bar{2}$) twins sometimes need an appreciable period to progress, over a few seconds. While twinning dislocation has not been confirmed to exist in this crystal, twinning should progress by the generation and motion of twinning dislocations. The amounts of shear are 0.384 and 0.658 for the (120) and (12 $\bar{2}$) twinings respectively. The elastic energy of dislocation is proportional to the square of Burgers vector corresponding to the shear of twin. The square of shear of the (12 $\bar{2}$) twinning is about three times as large as that of (120) twinning. Hence, the (12 $\bar{2}$) twinning needs longer period for the accumulation of the strain energy for the dislocation motion. Further, the K_2 plane is not the surface plane in the (12 $\bar{2}$) twin; surface rearrangement on twinning may drag the progress of the twinning.

The SEM, X-ray topography and Laue photograph show that the twin is coherent with the mother crystal without any strain; the twin boundary is sharp and narrow, less than 0.1 μm . In low molecular weight materials, twin boundary is sharp in the atomic scale. In polymer crystals, each molecules are bound by covalent bonds, and hence it is difficult to avoid steric hindrance during the twinning. In particular, PTS molecule has big side groups which prevent the chains from rearranging and forming the sharp boundary. The twin boundary of a PTS polymer crystal may therefore have a finite width. Hence, the definite fact is that the polymer chains must bend at the twin boundary whether the twin boundary is sharp or not.

If the polymer has only the acetylenic structure (Fig. 1b), the chain axis would not change its direction; allowed rotation around the single bond of the backbone cannot bend the chain. At the twin boundary, the back bones should therefore have butatrienic structure, which some parts of the polymer have been reported to have⁹⁾; in this case, the chain can bend by the rotation at the single bond shown by an arrow (Fig. 1b).

If butatrienic backbones arrange in the particular part of the undeformed crystal, they may form the nucleus of twin. When shear stress is applied, the butatrienic backbones kink at the single bonds to induce the twin and twinning dislocations. For the growth of the twin, acetylenic backbones should transform to butatrienic ones by the stress of the twinning dislocation; the butatrienic back bones kink one by one and arrange on the twin boundary with the motion of the twinning dislocation. The arrangement of the butatrienic back bones on twin boundary may be confirmed by optical

absorption if dense twin layers could be induced.

High resolution electron microscopy will give the detailed structure of the twin boundary and may determine the definite mechanism of the twinning.

In the present study of the deformation of PTS polymer crystals, only twinning has occurred; no plastic deformation by slip and phase transition has been observed. Slip may occur by other deformation modes such as stretching. It is also expected that resolved shear reverse to that inducing the twins may introduce phase transitions.

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